

# AMENDED SPECIFICATION

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## PATENT SPECIFICATION

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1,078,234



NO DRAWINGS

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### COMPLETE SPECIFICATION

#### Polyarylene Polyethers

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignee of ROBERT NORMAN JOHN-SON and ALFORD GAILEY FARNHAM), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a class of organic polymers having etheric oxygen valently connecting together aromatic nuclei or residuum of aromatic compounds. These polymers are appropriately termed polyarylene polyethers. More particularly, this invention relates to high molecular weight polyarylene polyethers as new polymers per se and to a method for the preparation of such polymers, which polymers are characterized by excellent high temperature resistance, toughness and stability.

Heretofore, temperature resistance of organic polymers has been a limiting factor to the broad use of polymers in end uses where high temperatures are encountered either intermittently or continuously. In fact only several known polymers are acceptable for use where ambient temperatures exceed 100°C., and the majority of these are thermoset products. Other thermoplastic resins known for use at such temperatures also create problems of handling, forming, stability, or else are extremely expensive or difficult to prepare.

The need is obvious for a thermoplastic polymer that is relatively inexpensive, easy to extrude and form into shaped objects, and yet has excellent toughness, temperature resis-

[Price

tance and form stability at elevated temperatures. 40

It has now been discovered that high molecular weight polyarylene polyethers possess this combination of desirable properties.

Accordingly, high molecular weight polyarylene polyethers of the present invention are composed of recurring units having the formula 45



wherein E is the residuum of the dihydric phenol, as hereinafter defined, and E' is the residuum of a benzenoid compound, as hereinafter defined having an inert electron withdrawing group in at least one of the positions ortho or para to the valence bonds and where both of said residua are valently bonded to the ether oxygen through aromatic carbon atoms, as hereinafter more fully discussed. Polymers of this type exhibit excellent strength and toughness properties as well as outstanding thermal, oxidative, and chemical stability. They find wide utility in the production of shaped and molded articles where such properties are necessary and are highly desirable, and also in the preparation of film and fiber products which have excellent mechanical properties even in the unoriented condition. Orientation by conventional and known techniques even further improves these mechanical properties in providing films and fibers having strengths heretofore unobtainable in organic polymers. 50 55 60 65 70 75

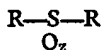
The invention also comprises the process for the preparation of polyarylene polyethers by the reaction of a double alkali metal salt of a dihydric phenol with a dihalobenzenoid com-

pound having an inert electron withdrawing group in at least one of the positions ortho or para to the halogen atoms under anhydrous conditions, and in the liquid phase of an inert, highly polar organic solvent. Catalysts are not necessary for this reaction but the unique facility of these solvents to promote the reaction to a high molecular weight product has now provided the critical tool necessary to secure sufficiently high molecular weight aromatic ether products useful for services heretofore limited to such products as polyformaldehydes and polycarbonates.

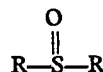
In another aspect of this invention, the polymers are also prepared in a process in which a dihydric phenol is first converted *in situ* in the primary reaction solvent to the alkali metal salt by the reaction with such alkali metal agents as per se, alkali metal hydrides, alkali metal hydroxides, alkali metal alkoxides or alkali metal alkyl compounds. Preferably, the alkali metal hydroxide is employed and after removing the water which is present or formed, in order to secure anhydrous conditions, stoichiometric quantities of the dihalobenzenoid compound are admixed and reacted to the high polymer. Likewise, the same result is achieved by adding the alkali metal salt of the dihydric phenol in the solvent to the dihalobenzenoid compound either continuously, incrementally or all at once so as to achieve the polymerization reaction. Thus, the reaction can readily be conducted in batch, semi-continuous, or continuous operation by the proper selection or adjustment of addition rate, reaction rate and temperature as is obvious to those skilled in the art from the present disclosure.

The polymerization reaction proceeds in the liquid phase of a highly polar inert organic solvent at elevated temperatures, as herein-after more fully set forth. While it has been found that the alkali metal salt of the dihydric phenol has only limited solubility in these solvents, this feature provides for easy control of the reaction and if desired, the slow addition of one reactant to the other to provide satisfactory high molecular weight polymers.

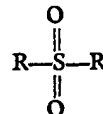
Examples of such solvents as heretofore mentioned as those of the formula:



in which each R represents a monovalent lower hydrocarbon group free of aliphatic unsaturation on the alpha carbon atom, and preferably contains less than about 8 carbon atoms or when connected together represents a divalent alkylene group with z being an integer from 1 to 2 inclusive. Thus, in all of these solvents all oxygens and two carbon atoms are bonded directly to the sulfur atom. Thus, contemplated for use in this invention are such solvents as those having the formula



and



where the R groups are lower alkyl, e.g. methyl, ethyl, propyl and, butyl and aryl groups, e.g. phenyl and alkyl phenyl groups, as well as those where the R groups are interconnected as in a divalent alkylene bridge, e.g.



as in thiophene oxides and dioxides. Specifically mentionable of these solvents but by no means exhaustive of those solvents are dimethylsulfoxide, dimethylsulfone, diethylsulfoxide, diethylsulfone, diisopropylsulfone, tetrahydrothiophene 1,1-dioxide (commonly called tetramethylene sulfone or sulfolane) and tetrahydrothiophene-1 monoxide. The dimethylsulfoxide has been found to be the most useful as the solvent for this reaction because it is a solvent for the widest variety of reactants as well as for the resulting polymer produced in the reaction. Aliphatic unsaturation on the  $\alpha$  carbon atom, such as occurs in divinyl sulfone and sulfoxide, should not be present as such materials tend to be reactive and polymerize under the conditions of this reaction. However, unsaturation on a  $\beta$  carbon atom or one further removed from the sulfur atom can be tolerated and such solvents can be employed in this reaction.

It is essential in the polymerization reaction that the solvent be maintained anhydrous before and during the reaction. While amounts of water up to about one per cent can be tolerated, and are somewhat beneficial when employed with fluorinated dihalobenzenoid compounds, amounts of water greater than this are desirably avoided as the reaction of water with the dihalobenzenoid compound leads to formation of phenolic species and only low molecular weight products are secured. Owing to the nature of the polymerization reaction of the dihalobenzenoid compound with an equimolar amount of the alkali metal salt of the dihydric phenol, this upset of the necessary stoichiometry limits the molecular weight obtainable. Consequently, in order to secure the high polymers, the reaction mixture should be substantially anhydrous, and preferably with less than 0.5 per cent by weight water in the reaction mixtures.

While such problems are avoided when using the dry crystalline alkali metal salt of the dihydric phenol, as the one reactant, it is often more convenient to form the alkali metal salt *in situ* in the reaction solvent, and thus employ the process described heretofore.

In situations where it is desired to prepare the alkali metal salt of the dihydric phenol *in situ* in the reaction solvent, the dihydric phenol and an alkali metal hydroxide are admixed in essentially stoichiometric amounts and normal precautions taken to remove all the water of neutralization, preferably by distillation of a water-containing azeotrope from the solvent-metal salt mixture.

It has been found convenient to employ benzene, xylene, halogenated benzenes or other inert organic azeotrope-forming organic liquids in performing this. Heating the alkali metal hydroxide, dihydric phenol, and small amounts of the azeotrope former to reflux for several hours while removing the azeotrope is the most desirable. However, it is obvious that any other technique for removing essentially all of the water can be equally satisfactory.

It is not essential and critical in this reaction that all of the azeotrope former be removed before the reaction of the alkali metal salt of the bisphenol with the dihalobenzenoid compound. In fact, it is desirable in some instances to employ an amount of such material in excess of that needed to azeotropically remove off all of the water, with the balance being used as a cosolvent or inert diluent with the principal solvent. Thus, for instance, benzene, heptane, xylene, toluene, chlorobenzene, and dichlorobenzene can be beneficially employed.

The azeotrope former can be one either miscible or immiscible with the major solvent. If it is not miscible it should be one which will not cause precipitation of the polymer in the reaction mass. Heptane is such a solvent. When employed, it will merely remain inert and immiscible in the reaction mass. If the azeotrope former would cause precipitation of the polymer, it should be removed almost completely from the reaction mass before initiating polymerization.

For such reasons, it is preferred to employ azeotrope formers which are miscible with the major solvents and which also act as cosolvents for polymer during polymerization. Chlorobenzene, dichlorobenzene and xylene are azeotrope formers of this class. Preferably the azeotrope former should be one boiling below the decomposition temperature of the major solvent and be perfectly stable and inert in the process, particularly inert to the alkali metal hydroxide when the alkali metal salt of the dihydric phenol is prepared *in situ* in the presence of the inert diluent or azeotrope former.

It has been found that chlorobenzene and o-dichlorobenzene serve particularly well as the

inert diluent and are able significantly to reduce the amount of the solvent necessary. The cosolvent mixture using as much as 50 per cent of the halogenated benzene with dimethylsulfoxide, for example, not only permits the formed polymer to remain in solution and thus produce high molecular weight polymers, but also provides a very economical processing mixture, and an effective dehydration operation. These materials are also completely stable to the alkali metal hydroxides employed in the *in situ* neutralization of the hydroxy groups of the dihydric phenol.

Any of the alkali metal hydroxides can be employed in this technique, that is to say any alkali metal salt of the dihydric phenol can be used as the one reactant. Potassium and cesium salts have been found to react considerably faster than the sodium salts, but due to expense of the cesium salts, the potassium salts are preferred. As heretofore indicated, the alkali metal salt should, of course, be the double metal salt, i.e. both aromatic hydroxyl groups being saponified, in order to prepare these products. Single metal salts ordinarily limit the molecular weight of the product. While this may be desirable as a chain terminator or molecular weight regulator near the terminus of the reaction period, the initial reaction and the major portion thereof should be with the double alkali metal salt of the dihydric phenol. The alkali metal moieties of this compound however can be the same or different alkali metals.

The residuum E of the dihydric phenol of these alkali metal salts is not narrowly critical. It can be, for instance, a mononuclear phenylene group as results from hydroquinone and resorcinol, or it may be a di- or polynuclear residuum. Likewise it is possible that the residuum be substituted with other inert nuclear substituents e.g. halogen, alkyl, and alkoxy substituents.

From a practical standpoint, limitations on polymer molecular weights may be expected when the dihydric phenol or the alkali metal derivative thereof contain strong electron withdrawing groups. This may result in lower molecular weight polymers or impractically slow reaction rates. Hence, it is preferred that the dihydric phenol be a weakly acidic dinuclear phenol, for example, the dihydroxy diphenyl alkanes or the nuclear halogenated derivatives thereof, for example, the 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)2-phenyl ethane, bis(4-hydroxyphenyl)methane, or the chlorinated derivatives containing one or two chlorines on each aromatic ring. While these halogenated bisphenolic alkanes are more acidic than the non-halogenated bisphenols and hence slower in reactivity in this process, they do impart valuable flame resistance to these polymers. Other materials also termed appropriately "bisphenols" are also highly valuable and preferred. These materials are the bisphenols of a

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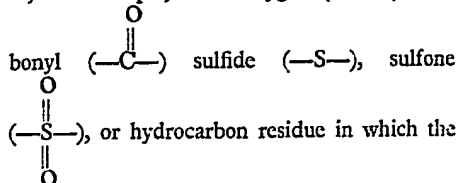
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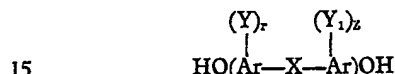
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symmetrical or unsymmetrical joining group, as, for example, ether oxygen ( $-\text{O}-$ ), car-



- 5 two phenolic nuclei are joined to the same or different carbon atoms of the residue, for example, the bisphenol of acetophenone, the bisphenol of benzophenone, the bisphenol of vinyl cyclohexene, the bisphenol of  $\alpha$ -pinene, 10 and bisphenols where the hydroxyphenyl groups are bound to the same or different carbon atoms of an organic linking group.

Such dinuclear phenols can be characterized as having the structure:



- wherein Ar is an aromatic group and preferably is a phenylene group, Y and  $\text{Y}_1$  can be the same or different inert substituent groups (e.g. alkyl groups having from 1 to 4 carbon atoms, halogen atoms, i.e. fluorine, chlorine, bromine or iodine, or alkoxy radicals having from 1 to 4 carbon atoms), and  $r$  and  $z$  are 0 or integers having a value from 1 to 4 inclusive, and X is representative of a bond between 25 aromatic carbon atoms as in dihydroxydiphenyl, or is a divalent radical, including

for example, inorganic radicals (e.g.  $-\overset{\text{O}}{\text{C}}-$ ,  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{S}-\text{S}-$ ,  $-\text{SO}_2-$ ), and 30 divalent organic hydrocarbon radicals e.g. alkylene, alkylidene, cycloaliphatic, or the halogen, alkyl, aryl substituted alkylene, alkylidene and cycloaliphatic radicals as well as alkalicyclic, alkarylene and aromatic radicals and a ring fused to both Ar group.

- 35 Examples of specific dihydric polynuclear phenols include among others: the bis-(hydroxyphenyl) alkanes, e.g., 2,2 - bis - (4-hydroxyphenyl)propane, 2,4' - dihydroxydiphenylmethane, bis - (2 - hydroxyphenyl) methane, bis - (4 - hydroxyphenyl)methane, bis(4 - hydroxy - 2,6 - dimethyl - 3 - methoxyphenyl)methane, 1,1 - bis - (4 - hydroxyphenyl)ethane, 1,2 - bis - (4 - hydroxyphenyl)ethane, 1,1 - bis - (4 - hydroxy - 2-chlorophenyl)ethane, 1,1 - bis - (3 - methyl - 4 - hydroxyphenyl)propane, 1,3 - bis - (3-methyl - 4 - hydroxyphenyl)propane, 2,2-bis - (3 - phenyl - 4 - hydroxyphenyl)propane, 2,2 - bis - (3 - isopropyl - 4 - hydroxyphenyl)propane, 2,2 - bis - (2 - isopropyl - 4 - hydroxyphenyl) - propane, 2,2 - bis - (4-

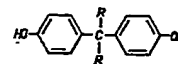
hydroxynaphthyl)propane, 2,2 - bis - (4-hydroxyphenyl)pentane, 3,3 - bis - (4-hydroxyphenyl)pentane, 2,2 - bis - (4-hydroxyphenyl)heptane, bis - (4 - hydroxyphenyl)phenylmethane, 2,2 - bis - (4-hydroxyphenyl) - 1 - phenyl - propane, and 2,2 - bis(4 - hydroxyphenyl)1,1,1,3,3,3 - hexafluoropropane;

di(hydroxyphenyl)sulfones, e.g. bis - (4-hydroxyphenyl) - sulfone, 2,4' - dihydroxydiphenyl sulfone, 5' - chloro - 2,4' - dihydroxydiphenyl sulfone, and 5' - chloro - 4,4' - dihydroxydiphenyl sulfone;

di(hydroxyphenyl)ethers, e.g. bis - (4-hydroxyphenyl)ether, the 4,3' -, 4,2' -, 2,2' -, 2,3' -, dihydroxydiphenyl ethers, 4,4' - dihydroxy - 2,6 - dimethyldiphenyl ether, bis - (4 - hydroxy - 3 - isobutylphenyl)ether, bis - (4 - hydroxy - 3 - isopropylphenyl)ether, bis - (4 - hydroxy - 3 - chlorophenyl)ether, bis - (4 - hydroxy - 3 - fluorophenyl)ether, bis - (4 - hydroxy - 3 - bromophenyl)ether, bis - (4 - hydroxynaphthyl)ether, bis - (4 - hydroxy - 3 - chloronaphthyl)ether, bis - (2 - hydroxyphenyl)ether, 4,4' - dihydroxy - 3,6 - dimethoxydiphenyl ether, and 4,4' - dihydroxy - 2,5 - diethoxydiphenyl ether.

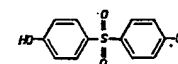
A preferred form of the polyarylene polyethers of this invention are those prepared using the dihydric polynuclear phenols of the following four types, including the derivatives thereof which are substituted with inert substituent groups

(a)

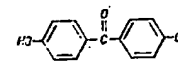


in which the R group represents hydrogen, lower alkyl, lower aryl and the halogen substituted groups thereof, which can be the same or different.

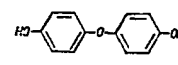
(b)



(c)



(d)



Thus, it is seen that the particular structure of the dihydric phenol moiety of the alkali metal salt reactant is not narrowly critical. However, as would be expected this moiety or

residuum in the polymer chain can alter or vary the properties of the resultant polymer produced. Similarly the reaction rate, optimum reaction temperature and like variables in the process can be varied by the selection of the particular dihydric phenol and the alkali metal salt thereof so as to give any desired change in rate, temperature, physical properties of the polymer and like changes.

It is also contemplated in this invention to use a mixture of two or more different dihydric phenols to accomplish the same ends as above. Thus when referred to above the —E— residuum in the polymer structure can actually be the same or different aromatic residuums.

As herein used the term "residuum of the (or a) dihydric phenol" means the residue of the dihydric phenol after the removal of the two aromatic hydroxyl groups. Thus as is readily seen these polyarylene polyethers contain recurring groups of the residuum of the dihydric phenol and the residuum of the benzenoid compound bonded through aromatic ether oxygen atoms.

Any dihalobenzenoid compound or mixture of dihalobenzenoid compounds can be employed in this invention which compound or compounds has the two halogens bonded to benzene rings having an electron withdrawing group in at least one of the positions ortho or para to the halogen groups. The dihalobenzenoid compound can be either mononuclear where the halogens are attached to the same benzenoid ring or polynuclear where they are attached to different benzenoid rings, as long as there is the activating electron withdrawing group in the ortho or para position of that benzenoid nucleus.

Any of the halogens may be the reactive halogen substituents on the benzenoid compounds. Fluorine and chlorine substituted benzenoid reactants are preferred; the fluorine compounds for fast reactivity and the chlorine compounds for the inexpensiveness. Fluorine substituted benzenoid compounds are most preferred, particularly when there is a trace of water present in the polymerization reaction system. However, as mentioned before, this water content should be maintained below about 1% and preferably below 0.5% for best results.

Any electron withdrawing group can be employed as the activator group in these compounds. It should be, of course, inert to the reaction, but otherwise its structure is not critical. Preferred are the strong activating

groups e.g. the sulfone group  $\begin{array}{c} \text{O} \\ || \\ \text{---S---} \\ || \\ \text{O} \end{array}$  bonding

two halogen substituted benzenoid nuclei, as in the 4,4'-dichlorodiphenyl sulfone and 4,4'-difluorodiphenyl sulfone, although such other

strong withdrawing groups hereinafter mentioned can also be used with equal ease.

The more powerful of the electron withdrawing groups give the fastest reactions and hence are preferred. It is further preferred that the ring contain no electron supplying groups on the same benzenoid nucleus as the halogen; however, the presence of other groups on the nucleus or in the residuum of the compound can be tolerated. Preferably, all of the substituents on the benzenoid nucleus are either hydrogen (zero electron withdrawing), or other groups having a positive sigma\* value, as set forth in J. F. Bunnett in Chem. Rev. 49 273(1951) and Quart. Rev. 12 1(1958).

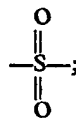
The electron withdrawing group of the dihalobenzenoid compound can function either through the resonance of the aromatic ring, as indicated by those groups having a high sigma\* value, i.e. above about +0.7 or by induction as in perfluoro compounds and like electron sinks.

Preferably the activating group should have a high sigma\* value, preferably above 1.0, although sufficient activity to promote the reaction is evidenced in those groups having a sigma\* value, i.e. above about +0.7 or by rate with such a low powered electron withdrawing group may be somewhat low.

The activating group can be basically either of two types;

(A) monovalent groups that activate one or more halogens on the same ring, e.g. a nitro group, phenylsulfone, or alkylsulfone, cyano, trifluoromethyl, nitroso, and hetero nitrogen as in pyridine.

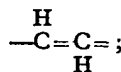
(B) divalent group which can activate displacement of halogens on two different rings, e.g. the sulfone group



the carbonyl group



the vinyl group



the sulfoxide group



the azo-group

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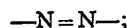
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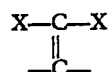
the saturated fluorocarbon groups



organic phosphine oxides



where R is a hydrocarbon group, and the ethylidene group



where X can be hydrogen or halogen or which can activate halogens on the same ring such as with difluorobenzoquinone, 1,4- or 1,5- or 1,8-difluoroanthraquinone.

If desired, the polymers may be made with mixtures of two or more dihalobenzenoid compounds each of which has this structure, and which may have different electron withdrawing groups. Thus the E' residuum of the benzenoid compounds in the polymer structure may be the same or different.

It will be seen that as used herein, the term "residuum or the (or a) benzenoid compound" means the aromatic or benzenoid residue of the dihalobenzenoid compound after the removal of the halogen atoms on the benzenoid nucleus. Thus, the residuum has an inert electron withdrawing group in at least one of the positions ortho or para to the valence bonds by which the residuum is bonded to the adjacent ether oxygen atoms; the residuum is valently bonded to the ether oxygen atoms through aromatic carbon atoms.

The reaction between the dihalobenzenoid compound and the alkali metal salt of the bisphenol proceeds on an equimolar basis. This can be slightly varied but a variation of more than 5 per cent away from equal molar amounts seriously reduces the molecular weight of the polymers. Since the desirable properties of these polymers are secured because of the high molecular weights achieved, equal molar amounts are preferred.

The reaction of the dihalobenzenoid compound with the alkali metal salt of the dihydric phenol readily proceeds without need of an added catalyst upon the application of heat to such a mixture in the selected sulfone or sulfoxide solvent. Inasmuch as the polymerization reaction is conducted in the liquid phase of the solvent, the selected reaction temperature should be below the ambient boiling point of solvent and above its freezing point. Such solvents as dimethyl sulfone and tetramethylene sulfone (sulfolane) freeze at about

room temperatures, it is obvious that with such materials, elevated temperatures are desirable.

Also desirable is the exclusion of oxygen from the reaction mass to avoid any possibility of oxidative attack to the polymer or to the principal solvent during polymerization particularly at the higher temperatures. Nitrogen blanketing the reaction flask serves this purpose very well.

While the reaction temperature is not narrowly critical, it has been found that at temperatures below about room temperature, the reaction time is inordinately long in order to secure high molecular weights. The higher temperatures i.e. above room temperature and generally above 100°C., are much more preferred for shorter processing times and for a more economical system. Most preferred are temperatures between about 120°C. to 160°C. Higher temperatures can of course be employed, if desired, provided that care is taken to prevent degradation or decomposition of the reactants, the polymer and the solvents employed. For example, dimethylsulfoxide is known to decompose at its boiling point, i.e. about 189°C. Consequently, it is desired to the reaction temperature below this to avoid such problems when employing this solvent.

Temperatures higher than 100°C. are preferred in order to keep the polymer in solution during the reaction since the sulfoxide and sulfone solvents are not particularly good solvents for the polymer except in the hot condition. It is the feature of this process that high molecular weights are possible only when the growing polymer chain is dissolved in the solvent. Once the polymer precipitates from the solvent, its growing ceases, although it has also been found that when this happens, the addition of a second cosolvent as hereinbefore mentioned to the reaction or by increasing in reaction temperature, the precipitated polymer can be resolvated and the polymerization continued to higher molecular weights. Among such other cosolvents as might be mentioned for use solely to increase the fluidity of the reaction mass are diphenyl ether, anisole, xylene, chlorobenzene and dichlorobenzene even though other azeotrope formers may have previously been used or are still in are still in the reaction mass.

The reaction temperature can be effectively increased even above the normal boiling point of the solvent or mixture of solvents by the use of pressure in the reaction vessel. However, for most practical reactions contemplated herein, atmospheric pressures are quite adequate, though if desired pressures as high as 1000 psig, or more can be employed.

Preferably the polymerization reaction mass is a true solution at the reaction temperature except for by-product inorganic salt which is generally insoluble in the reaction mass. However, the reaction can still proceed as a swollen gel of solvent and dissolved polymer if high

solids reaction conditions are desired. This of course depends on the amount of solvent initially present and on the power of the agitator in the vessel. Desirably, it has been found that equal parts by weight of solvent and of total reactants seem to give optimum results. However if adequate stirring is provided and means are available for stripping the solvent from the polymer mass are provided, as little as one part solvent to five or more parts total reactants can still be desirable. Since these sulfone and sulfoxide solvents are quite expensive it is desired to use as little as possible, and preferably to use a cosolvent or inert diluent to provide sufficient fluidity to the reaction mass.

If however the polymer precipitates from the solvent at the reaction temperature, and such polymer is found to be of sufficiently high molecular weight for the intended end use, the reaction mass is actually a mixture of the solvent having the reactants dissolved therein and the precipitated polymer. However as stated previously this technique does not make as high a molecular weight as when the polymer remains dissolved in the reaction medium.

The polymer is recovered from the reaction mass in any convenient manner, such as by precipitation induced by cooling the reaction mass or by adding a nonsolvent for the polymer, or the solid polymer can be recovered by stripping off the solvent at reduced pressures or elevated temperatures.

Molecular weight of the polymer can be easily controlled in this process by the addition of a precipitating solvent to the reaction mixture when the desired reduced viscosity of the resin is secured or when the indicated viscosity of the polymerization mass is high enough to indicate the desired molecular weights are achieved. It is also possible to terminate the growing polymer chain by the addition of a monofunctional chain stopper, e.g. an alkyl halide or other suitable coreactant.

Since the polymerization reaction results in the formation of the alkali metal halide on each coupling reaction, it is preferred either to filter the salts from the polymer solution or to wash the polymer substantially to free it from these salts. For such reasons, the precipitation of the polymer from the reaction mass as a fluffy powder or fine granule is preferred, although chain termination is also beneficial in yielding a more stable polymer.

The polymers are characterized by high molecular weights that are not securable by any other known process or technique. The molecular weight of these polymers is indicated by reduced viscosity in indicated solvents. As well understood in the art, the viscosity of a resin solution bears a direct relationship to the weight average molecular size of the polymer chains, and is the most important single property that can be used to characterize the degree of polymerization. The

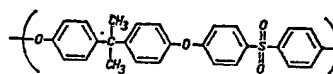
reduced viscosity limitation assigned to the polymer masses of the present invention are therefore to be understood as significant in reflecting molecular size rather than consideration concerning the viscosity *per se*. It will further be obvious that reduced viscosity values used herein are of significance only relative to each other rather than in any absolute sense, and for this reason other polyether-solvent mixtures can be employed as an indication of the relative molecular weight of these polymers. When solvents other than chloroform are employed, the required average molecular size relationship can readily be established by reference to the reduced viscosity values defined herein even though the numerical reduced viscosity values of the alternative solvents may be different.

Most of these polymers have indicated ready solubility in chloroform, or tetrachloroethane or other similar solvent. In all instances, the reduced viscosity above about 0.35 is an indication of a tough, strong fiber- or film-forming polymer with those having a reduced viscosity above about 0.4 being most preferred.

In a preferred manner of producing the polymer in accordance with this invention, bisphenol A, 2,2-bis(4-hydroxyphenyl) propane, is added to a mixture of dimethylsulfoxide and benzene (as an azeotroping agent) in about a 50:50 ratio, using about 2 to 4 parts total solvent per part by weight of bisphenol A. Two molar equivalents of potassium hydroxide are then added and the mixture refluxed for 3-4 hours (ca. 110°C-130°C) while continuously removing the benzene-water azeotrope or until the mixture contains less than about 0.5 per cent by weight water and about 10 per cent by weight benzene.

An amount of difluorodiphenylsulfone equivalent to the molar amount of bisphenol A is then added and the resultant mixture maintained at 120°C-160°C. for  $\frac{1}{2}$  to 2 hours, or until the solution becomes too viscous to stir. After the desired reduced viscosity is reached, preferably 0.4, the polymer chains are terminated with methyl ether groups by the addition of a small amount of methyl chloride, and water added to precipitate the polymer. It is washed with methanol and/or water and dried.

Essentially quantitative yields of polymer containing units having the structure

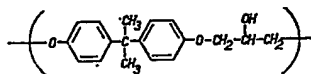


are secured (ca 98% yield or better). The product is practically free of by-products and is normally a colorless to slight amber, transparent resin. Typical physical properties are shown in the appended examples.

Comparative physical properties with other

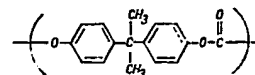
known high performance polymers are shown in the following Table I in which the polyhydroxyether is a bisphenol A polyhydroxyether containing units of the formula

5



and the polycarbonate is a bisphenol A poly-

carbonate containing units of the formula



sold under the name Lexan by the General Electric Co.

10

TABLE I

	Polyarylene polyether	Polyhydroxy- ether	Polycarbonate
Tensile Modulus, psi	300,000	280,000	300,000
Tensile Strength, psi.	10,500	8,000	10,000
Elongation to break %	30—100	50—100	80—130
Pendulum Impact, ft.lb./in <sup>2</sup>	100—200	100—150	400
Tg °C.	200°	95—100	150
TCU °C.*	175	95	110
Heat Distortion (264 psi)	174	95	135

\*TCU-continuous use temperature.

As can be readily seen, this polymer is outstanding in its continuous use temperature range and in the high heat distortion temperature.

15

One of the other outstanding properties of these polymers are the retention of toughness down to very low temperatures as well as its

good high temperature properties as well as heat aging characteristics as shown in Tables II, III and IV for the polymer as in Table I. In Table II, comparison of physical properties at higher temperatures with the bisphenol A polycarbonate shows the polyarylene polyether to be significantly superior.

20

25

TABLE II

Temp. °C.	Tensile Modulus, psi.		Tensile Strength, psi.	
	Polyarylene Polyether	Polycarbonate	Polyarylene Polyether	Polycarbonate
+100	220,000	170,000	6,500	5,000
+125	190,000	160,000	5,900	5,000
+150	170,000	20,000	4,000	1,500
+175	165,000	softened	3,000	softened
+200	1200	—	100	—



TABLE III

Mechanical Properties as a Function of Temperature  
for the Polyarylene Polyether

Temp. °C. <sub>a</sub>	Pendulum Impact ft.lbs./in. <sup>3</sup> *	Tensile Modulus psi.	Tensile Strength psi.	Elongation to Break %
-196	23	—	—	—
-175	25	370,000	20,000	9
-150	27	340,000	19,500	12
-125	74	338,000	16,500	10—30
-100	84	300,000	15,000	20—40
-75	100	300,000	14,500	65
-50	120	300,000	12,000	75
-25	120	275,000	10,500	75
-0	130	280,000	9,500	110
+25	200	260,000	9,000	130
+50	—	220,000	7,000	160
+75	—	220,000	7,000	185
+100	—	220,000	6,500	100
+125	—	190,000	5,900	45
+150	—	170,000	4,000	5
+175	—	165,000	3,000	2
+200	—	1,200	100	150

\*At room temperature polystyrene = 5 ft. lbs./in.<sup>3</sup>  
polypropylene = 50 ft. lbs./in.<sup>3</sup>

TABLE IV

Illustration of Melt Stability Exhibited by the Polyarylene Poether

Temp. 300°C.						
Time (min.)	0	20	60	90		
Melt Flow (dg./min.) 220 psi	—	1.9	1.8	1.8		
Red. Viscosity	0.70	0.69	0.69	0.69		
Temp. 325°C.						
Time	0	20	50	100	125	190
Melt Flow dg./in. (44 psi)	—	0.50	0.50	0.50	0.51	0.63
Red. Vis.	0.70	0.69	0.70	0.70	0.69	0.68
Temp. 350°						
Time	0	30	70	120	180	
Melt Flow (dg./min (44 psi)	—	1.5	1.6	1.7	2.3	
Red Visc..	0.70	0.70	0.69	0.66	0.65	

The electrical properties, e.g. dielectric constant, power factor, are better than the bisphenol A polycarbonate resin and a permeability to carbon dioxide, oxygen, hydrogen and nitrogen equivalent to the bisphenol A polycarbonate.

Creep resistance of the polymer is outstanding at 100°C. (loaded at 1% of tensile modulus) and appears to be far superior to any presently known polymers.

Contact of the polymer with boiling water, boiling 5% NaOH or boiling 5% sulfuric acid for 52 hours, 13 hours and 20 hours respectively shows no change whatsoever in any physical property. Only certain chlorinated solvents, i.e. chloroform, tetra chloroethane, methylene chloride, or cyclic ethers, i.e. tetrahydrofuran, dioxane, thiophene or higher polar solvents, e.g. nitrobenzene, p-chlorophenol, pyrrolidone, attack the polymer through dissolution. Ordinary aliphatic solvents, ketones, alcohols, nitriles or acetic acid have no effect on the polymer and do not dissolve it. The polymer is also free of stress crazing or environmental stress rupture even after 5 months in caustic soda, sulfuric acid, kerosene, oil, or synthetic detergents. Testing under 1500 psi tensile stress in an air oven at 150°C. showed the polymer to be basically unchanged after 900 hours.

Thus as is evident, these polymers are widely applicable to any desired end use in which such properties are desirable or necessary. Films and fibers made from these polymers are extremely tough and offer service over a wide range of use temperatures. Molded or extruded shapes of any sort can be made

from these polymers by conventional techniques well known in the art. However, since these polymers have fairly high glass transition temperatures, forming temperatures are somewhat higher than those employed for polypropylene, or polycarbonate resins.

In the appended Examples, the physical tests employed in measuring the properties of these were those as described in ASTM test method D-638-58T for tensile modulus, tensile strength, elongation to break, yield strength and yield elongation. Melt index was determined by ASTM test D-1238-57T.

Reduced viscosity (R.V.) as used herein was determined by dissolving a 0.2 gram sample of thermoplastic polyarylene polyether in the indicated solvent contained in a 100 ml. volumetric flask so that the resultant solution measured exactly 100 ml. at 25°C. in a constant temperature bath. The viscosity of 3 ml. of the solution which had been filtered through a sintered glass funnel was determined in an Ostwald or similar type viscometer at 25°C. Reduced viscosity values were obtained from the equation:

$$\text{Reduced Viscosity} = \frac{t_s - t_0}{c \cdot t_0}$$

wherein:  $t_0$  is the efflux time of the pure solvent

$t_s$  is the efflux time of the polymer solution

$c$  is the concentration of the polymer solution

expressed in terms of grams of polymer per 100 ml. of solution.

Glass transition temperature ( $T_g$ ), commonly referred to as second order phase transition temperatures, refers to the inflection temperatures found by plotting the resilience (recovery from 1 per cent elongation) of a film ranging in thickness from 3—15 mils against the temperature. A detailed explanation for determining resilience and inflection temperature is to be found in an article by Alexander Brown "Textile Research Journal" volume 25, 1955, at page 891.

Pendulum impact was measured by ASTM test method D-256-56 modified as follows: A steel pendulum was used, cylindrical in shape with a diameter of 0.85 inch and weighing 1.562 pounds. The striking piece, mounted almost at the top of the pendulum was a cylinder 0.3 inch in diameter. Film specimens, 1—1.5 inches long, 0.125 inch wide and about 1 to 20 mils thick were clamped between the jaws of the tester so that the jaws were spaced 1 inch apart. The 0.125 inch width of the film was mounted vertically. The pendulum was raised to a constant height to deliver 1.13 foot pounds at the specimen. When the pendulum was released the cylindrical striking piece hit the specimen with its flat end, broke the film, and traveled to a measured height beyond. The difference in the recovery height (i.e., the difference in the potential energy of the pendulum at the maximum point of the upswing) represents the energy absorbed by the specimen during rupture. The impact strength, expressed in foot-pounds per cubic inch, is obtained by dividing the pendulum energy loss by the volume of the specimen. Five to ten specimens are tested for each material.

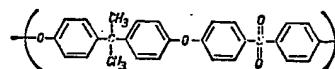
The following examples are illustrative of this invention. Unless otherwise indicated, all parts and percentages are by weight.

#### Example I

In a 250 ml. flask equipped with a stirrer, thermometer, a water-cooled condenser and a moisture trap filled with benzene, there were placed 11.42 grams of 2,2-bis(4-hydroxyphenyl)propane (0.05 moles), 13.1 grams of a 42.8% potassium hydroxide solution (0.1 moles KOH), 50 ml. of dimethylsulfoxide and 6 ml. benzene and the apparatus purged with nitrogen to maintain an inert atmosphere over the reaction mixture. The mixture was re-

fluxed for 3 to 4 hours, continuously removing the water contained in the reaction mixture as an azeotrope with benzene and distilling off enough of the latter to give a refluxing mixture at 130—135°C., consisting of the dipotassium salt of the 2,2-bis(4-hydroxyphenyl)propane and dimethylsulfoxide essentially free of water. The mixture was cooled and 14.35 grams (0.05 mole of 4,4'-dichlorodiphenylsulfone) were added followed by 40 ml. of anhydrous dimethylsulfoxide, all under nitrogen pressure. The mixture was heated to 130°C. and held at 130—140°C. with good stirring for 4—5 hours. The viscous, orange solution was poured into 300 ml. water, rapidly circulating in a Waring Blendor, and the finely divided white polymer was filtered and then dried in a vacuum oven at 110°C. for 16 hours. The yield was 22.2 grams (100% yield) and the reaction was 99% complete based on a titration for residual base. The reduced viscosity as measured in chloroform (0.2 gram polymer in 100 ml. at 25°C.) was 0.59.

The polymer had units of the formula



A substantial portion of the polymer was dissolved in 100 ml. tetrachlorethane and washed with dilute acetic acid and then water. After reprecipitation by pouring into 400 ml. of methanol, the polymer was filtered and dried in the vacuum oven at 70°C. Films prepared by compression molding the powder at 270°C. and 2—3000 psi. pressure gave the following properties:

Tensile Modulus	293,000 psi.
Tensile Strength	10,200 psi.
Elongation to break	7%
Pendulum Impact	50 ft.-lbs./cu. in.

In order to determine the resistance of this polymer to various environments, small samples of powdered polymer prepared in the same manner and having an initial R.V. of 0.65 were exposed for the indicated times in the following liquids, and also in a hot air oven.

Treatment	Time	Reduced Viscosity in Chloroform
None	—	0.65
Boiling Water	51 hours	0.65
5% Boiling NaOH	12 hours	0.65
5% Boiling H <sub>2</sub> SO <sub>4</sub>	20 hours	0.65
Air 259°C.	5 hours	0.64

The above shows that the polymer is highly stable at elevated temperatures to these indicated environments.

- 5 Films were extruded from a similarly prepared white polymer having a reduced viscosity in chloroform of 0.49, and a melt flow of 3.0 dg./min. (measured at 310°C. and 44psi.) by extrusion through a 1-5/8 inch diameter electrically-heated tubing die on a conventional 1.5 inch screw driven extruder. 10 The extruder was run at 275°—290°C. in the back zone and 290°—310°C. Using a normal compression-type screw (polyethylene type) it was found desirable to "starve feed" the 15 extruder. This prevented overloading the extruder drive and stalling the equipment. Screw speed was 28 r.p.m. The 1-5/8" diameter extrudate (40 mil thick) was blown 20 directly at the die face to a cylinder 8" to

9" in diameter. It was drawn down in the machine direction as well as transversely to a final gage of 1/2 to 3 mils, depending upon the particular draw down speed used. About 15 pounds of polymer were extruded into the various thicknesses of film. 25

The film exhibited very little molecular orientation since the film was blown at such a high (270°C.) temperature above the 190°C. second order temperature. The tubular film 30 was collapsed using the "ironing section" of the tubular film apparatus to give wrinkle-free film when the maximum heat was used in this section. The high second order temperature required additional heater capacity on the unit 35 to insure adequate ironing out of the collapsing wrinkles.

The properties of the 1.5 mil film prepared as above described are as follows:

	*M.D.	*T.D.
Tensile Modulus, psi.	290,000	266,000
Tensile Strength, psi.	9,600	7,800
Yield Strength, psi.	9,000	7,650
Yield Elongation, %	5.0	4.5
Ultimate Elongation, %	167	25—125

\* 'M.D.' means machine direction; 'T.D.' means transverse direction.

The film was clear, transparent, glossy and tough. It has high uninitiated and initiated tear strength.

#### Example II

- 45 A slurry of 45.64 grams of the disodium hexahydrate salt of 2,2-bis(4-hydroxyphenyl)propane (0.12 mole) in 100 ml. toluene, contained in a reaction flask as described in Example I, was refluxed with stirring for 2 hours during which time 13 ml. water were 50 collected in the trap. About 35 ml. toluene were distilled off, and then 125 ml. sulfolane (tetra-

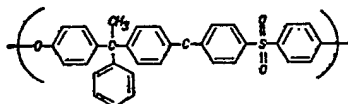
methylene sulfone) as the polar solvent were added and toluene further distilled off until a total of 80 ml. had been removed and a pot temperature of 210°C. was reached. This 55 resulted in a smooth slurry of finely divided white disodium salt of bisphenol A in anhydrous sulfolane.

The mixture was cooled and 34.66 grams 60 bis(4-chlorophenyl)sulfone (0.12 mole) added. The mixture was then heated 1 1/2 hours at about 220—225°C. The viscous polymer solution was cooled to 190—200°C. and treated 65 with methyl chloride then cooled further and

diluted with 125 ml. chlorobenzene. The diluted reaction mixture was filtered to remove salt and precipitated in alcohol in a Waring Blender. The polymer was dried in a vacuum oven overnight at 150°C. The yield was 46 grams and the reduced viscosity in chloroform was 0.53. The polymer had the same structure as in Example I.

#### Example III

This example was conducted in the same manner as Example I except 1,1-bis-(4-hydroxyphenyl)-1-phenyl ethane (bisphenol of acetophenone) was used as the dihydric phenol. The reaction time was 10 hours at 130—140°C. and the reduced viscosity in chloroform was 0.54. At the conclusion of the reaction, a solution of 0.5 gram methyl chloride in 6 ml. dimethylsulfoxide was added at 90—100°C. to convert unreacted aryloxy end-groups to the more stable aryl methyl ether end-groups. It had units of formula:



Clear, tough films were made by compression molding the powdered polymer at 280°C. at 2—3000 psi. room temperature. The mechanical properties are:

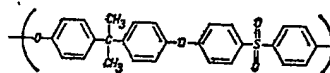
Tensile Modulus	325,000 psi.
Tensile Strength	11,000 psi.
Elongation to Break	6—20%
Pendulum Impact	50 ft-lbs/cu. in.
Tg.	200°C.

If desired the alkali metal salt of the dihydric phenol is also prepared *in situ* by the slow addition of the alkali metal precursor to a mixture of the other reactants in the solvent as is exemplified by the following example. That a high molecular weight polymer was secured is evidenced that the reaction involves the double alkali metal salt, even though during the slow addition of the base, the actual reaction could also involve the monosalt as well.

#### Example IV

Into a 250 ml. flask equipped with stirrer, thermometer addition funnel and reflux condenser were added 11.72 grams (0.0514 moles) of 2,2-bis(4-hydroxyphenyl)propane, 14.72 grams (0.0512 mole) of 4,4'-dichlorodiphenylsulfone and 50 ml. of dimethylsulfoxide under nitrogen pressure. The mixture was heated to 90°C. and 48.8 ml. of a solution of potassium t-butoxide in dimethylsulfoxide (2.13 molar solution) constituting 0.104 moles of potassium t-butoxide, were slowly added over ca. 4 hours with most of the base being added in the first

hour. The solution was heated to 130°C. and held at 120—130°C. for 4 hours. After recovering and washing the polymer as in Example I, the yield of polymer was 100% and had a reduced viscosity of 0.44 in chloroform, and units of the formula:

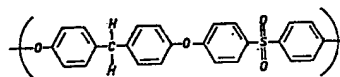


Compression molded films gave the following results on physical testing:

Tensile Modulus	390,000 psi.
Tensile Strength	11,300 psi.
Elongation to Break	5%
Pendulum Impact	45—90 ft-lbs/cu. in.
Tg.	190—200°C.

#### Example V

This example was conducted in the same manner as Example I except that dihydric phenol employed was 4,4'-dihydroxydiphenylmethane and the reaction temperature and time were 130—135°C. and 7 hours respectively. The reduced viscosity of the polymer (measured as a 0.2 gram sample in chloroform was 0.65. It had units of the formula

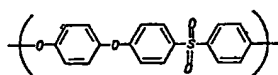


Tough, transparent films were cast from chloroform solution prepared by dissolving 8 grams of polymer in 65 ml. chloroform and casting the viscous solution onto a glass plate with a 19 mil doctor blade. The prepared films were air dried and then placed in an oven overnight at 140°C. The clear films were readily lifted off the glass plate and were found to be one mil thick. The following physical properties were obtained on this film.

Tg.	180°C.
Tensile Modulus	270,000 psi.
Tensile Strength	8,400 psi.
Elongation to Break	85%
Pendulum Impact	80 ft-lbs/cu. in.

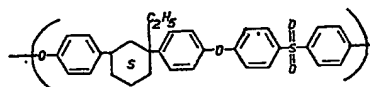
#### Example VI

This example was conducted in the same manner as Example I except hydroquinone was used as the dihydric phenol and the reaction was conducted at 130—140°C. for 6 hours. The reduced viscosity was 0.45 (p-chlorophenol at 25°C.) The resin melted at about 310°C. and tough films were prepared by melt pressing the polymer at 300—320°C. The polymer had units of the formula



#### Example VII

This example was conducted in the same manner as Example I except that 1,3-bis(p-hydroxyphenyl)-1-ethylcyclohexane (the bisphenol prepared by acid catalyzed condensation of 2 moles of phenol with one mol vinyl cyclohexene) was used as the dihydric phenol. The reaction was conducted for 7 hours at 130–140°C. after which the polymer was precipitated, washed, and dried as in Example I. Clear, tough films were made by compression molding at 330°C. and 2–3000 psi, and by casting from chloroform. The polymer had a reduced viscosity of 0.74 in chloroform and had units of the formula

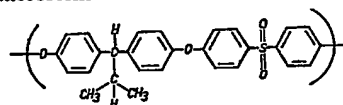


Some mechanical properties are:

Tensile Modulus	310,000 psi.
Tensile Strength	9,100 psi.
Elongation to Break	100–125%
Pendulum Impact	100 ft-lbs/cu. in.
Tg.	230°C

#### Example VIII

This example was conducted in the same manner as in Example I except that the dihydric phenol was 1,1-bis(4-hydroxyphenyl)-2,2-dimethylethane. (Bisphenol of isobutyraldehyde). The reaction was conducted for 7 hours at 130–135°C. after which the polymer was recovered, washed, and dried. The polymer had a reduced viscosity of 0.49 in chloroform and had units of the formula



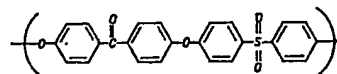
Clear, tough films were prepared by compression molding at 260°C. and 2–3000 psi. Mechanical properties of the film samples were as follows:

Tensile Modulus	275,000 psi.
Tensile Strength	9,400 psi.
Elongation to Break	6–15%
Pendulum Impact	68 ft-lbs/cu. in.
Tg.	200–205°C.

#### Example IX

This example was conducted in the same manner as the previous example except that the dihydric phenol was 4,4'-dihydroxybenzophenone. After 4½ hours reaction at 135–

145°C. the polymer was recovered, and had a reduced viscosity of 0.39 in chloroform. Compression molded films prepared at 290°C. and 2–3000 psi. were extremely tough and the polymer had units of the formula

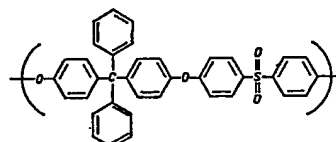


and the following physical properties:

Tensile Modulus	290,000 psi.
Tensile Strength	10,700 psi.
Elongation to Break	5–60%
Pendulum Impact	107 ft-lbs/cu. in.
Tg.	205°C.

#### Example X

This example was conducted in the same manner as the previous example except the dihydric phenol was 4,4'-(dihydroxyphenyl)diphenylmethane (bisphenol of benzophenone). After 20 minutes reaction at 110–127°C. the polymer was recovered and had units of the formula



and had a reduced viscosity in chloroform of 0.70. Films pressed at 330°C. and 2–3000 psi. were clear and had the following properties:

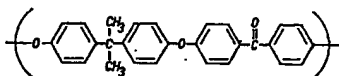
Tensile Modulus	350,000 psi.
Tensile Strength	8800 psi.
Elongation to Break	3–7%
Pendulum Impact	4–14 ft-lbs/cu. in.
Tg.	230°C.

#### Example XI

To a 500 ml. 3-necked flask equipped with a mechanical stirrer, a condenser attached to a moisture trap, temperature recording device and an inert gas inlet tube, there were added 22.84 grams of 2,2-bis(4-hydroxyphenyl)propane, 80 ml. benzene and 150 ml. distilled dimethylsulfoxide. With stirring, the dropwise addition of 21.49 grams potassium hydroxide solution (9.31 meq. KOH/gm.) was started. After completion of the KOH addition, the reaction mixture was heated to reflux and maintained there for about 5.5 hours, while continuously removing the benzene-water azeotrope to secure an anhydrous solution of the dipotassium salt of 2,2-bis(4-hydroxyphenyl)propane in the dimethylsulfoxide. After cooling to room temperature, 21.84 grams of 4,4'-difluorobenzophenone were

added. Heat was applied and soon the viscosity of the reaction mixture was observed to increase. About 30 minutes after addition of the difluorobenzophenone the polymer appeared to be out of solution and 40 ml. o-dichlorobenzene were added. The reaction had been heated from 25°C. to 135°C. during the thirty minute period. Eight minutes after the o-dichlorobenzene was added, methyl chloride addition was started in order to convert the terminal end groups to the more stable methoxy end groups. The gas was passed through the reaction mixture for five minutes and the reaction mixture was then allowed to cool to room temperature. The polymer separated from solution upon cooling.

About 250 ml. chloroform were added to the reaction mixture which tended to plasticize the polymer. The whole reaction mixture was then added to 21.7 grams ethanol in a large agitated vessel, filtered, and washed again in the blender with ethanol. After drying several hours in a vacuum oven at 105°C. the powder was washed twice with 2 liters of distilled water in the vessel. The white powder was then dried for several days in a vacuum oven at 100°C. The product weighed 36.2 grams and had a reduced viscosity of 1.0 (0.05 gram sample in 25 ml. tetrahydrofuran at 25°C). Films were prepared as in previous examples. The polymer had units of the formula:



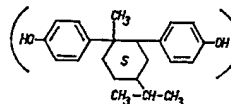
Properties obtained on compression molded films were as follows:

Tensile Modulus	270,000 psi.
Tensile Strength	9600 psi.
Elongation to Break	150%
Pendulum Impact	200—300 ft-lbs/cu. in
Tg.	155°C

#### Example XII

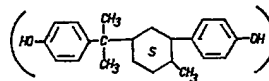
The preparation of the dipotassium salt of the bisphenol and azeotrope step was carried out in the same manner as Example XI except that 32.44 grams of  $\alpha$ -pinene bisphenol, prepared by the acid catalyzed condensation of phenol and  $\alpha$ -pinene, were substituted for the 2,2-bis(4-hydroxyphenyl)propane. The reflux was maintained for 4.75 hours to remove all the water.

This bisphenol is composed of a mixture of two specific position isomers, generally in a 2 to 1 molar ratio of  $\beta$ -bisphenol



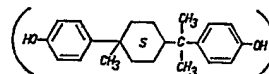
and  $\alpha$  bisphenol

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and is prepared by condensing 2 moles of phenol with one mole of  $\alpha$ -pinene in the presence of an acidic cation exchanging resin. Use of weaker acidic catalysts, e.g. aluminium chloride can form the  $\alpha$  bisphenol

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isomer from phenol and dipentene hydrochloride, if such is desired.

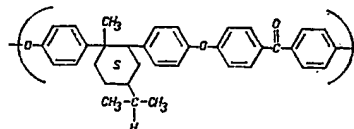
After adding the difluorobenzophenone, the reaction mixture was heated at about 130—140°C. for about 3 hours. Forty ml. of o-dichlorobenzene were added when the reaction temperature reached 130°C. Chain termination was again accomplished with methyl chloride for 5 minutes. Isolation in the manner of Example XI except that the reaction was not diluted with chloroform, gave 46.5 grams polymer as a white powder, with a reduced viscosity of 0.87 (0.05 gram sample in 25 ml. chloroform at 25°C.)

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The polymer had units of the formula for the bisphenol portion



Properties obtained on a compression molded film were as follows:

80

Tensile Modulus	245,000 psi.
Tensile Strength	9500 psi.
Elongation to Break	18—135%
Pendulum Impact	200—300 ft-lbs/cu. in.
Tg.	200°C.

85

#### Example XIII

In a 500 ml. flask equipped as in Example XI were placed 25.03 grams (0.10 moles) of 4,4'-dihydroxydiphenylsulfone, 100 ml. xylene and 21.47 grams of KOH solution. (9.31 meq. KOH per gram). A precipitate formed but dissolved when 150 ml. of tetrahydrothiophene-1,1-dioxide (commonly called

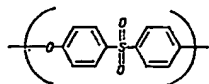
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“sulfolane” or tetramethylene sulfone, which had been vacuum distilled from NaOH) were added. The reaction mixture was heated to reflux and water removed through the moisture trap. Reflux was maintained for about 4 hours to remove all the water and form the dipotassium salt of the 4,4'-dihydroxydiphenylsulfone in an anhydrous solution of the sulfolane and xylene.

After cooling to 45°C., 28.76 grams (100 moles) of 4,4'-dichlorodiphenylsulfone were added and the reaction mixture, containing a precipitate, was heated to 240°C. Most of the xylene distilled off at 154–166°C. At 215°C. the reaction mixture nearly cleared. The yellowish reaction mixture was held at 240°C. for about 3.75 hours. It was then cooled to 160°C. and end-terminated with a small amount of methyl chloride.

After cooling to 50°C., the reaction mixture was coagulated in 2 liters ethanol in a large agitated vessel. The washing was repeated after filtration and then the powdery product was dried one hour at 100° in a vacuum oven. It was then washed in the vessel two times with 2 liters of distilled water, filtered, and dried overnight at 100°C. in a vacuum oven. In this manner 43.6 grams of white powdery polymer were obtained with a reduced viscosity of 0.48 (0.05 g./25 ml. of 1,1,2,2-tetrachloroethane at 25°C.).

The polymer had units of the formula

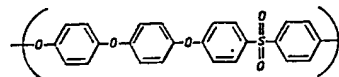


#### Example XIV

To a solution of 24.26 grams of 4,4'-dihydroxydiphenylether (0.12 mole) in 160 cc. dimethylsulfoxide and 45 cc. benzene in a 500 cc. reaction flask were added under a nitrogen atmosphere 25.25 grams 53.28% KOH (0.24 mole). The mixture was refluxed with stirring and the slow addition of nitrogen gas with removal of water by a moisture trap for a total of 5 hours. The mixture of solid potassium salt of 4,4'-dihydroxydiphenyl ether and solvent was cooled to room temperature and 34.46 grams 4,4'-dichlorodiphenylsulfone (0.12 mole) added. The reaction mixture was then warmed to about 130°C. for 3.5 hours during which time it became quite viscous. The mixture was cooled to 110°–120°C. and methyl chloride bubbled in for a short time to methylate any unreacted phenoxide groups.

The reaction mixture was cooled, dissolved in 200 cc. methylene chloride, washed with several portions of water, and the polymer solution precipitated into alcohol in an agitated vessel. After washing with alcohol and drying in a vacuum oven at 100°C. overnight the yield of polymer was 48 grams (calc. 49.9).

This polymer had a reduced viscosity of 0.53 (0.05 g./25 ml. chloroform at 25°C.) It had units of the formula



A film was compression molded at 260°C. at 2,000 to 3,000 psi. and exhibited the following properties.

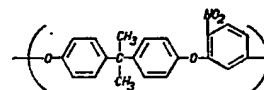
Tensile Modulus	270,000 psi.	
Tensile Strength	10,000 psi.	
Elongation to Break	72–200%	
Pendulum Impact	200–500 ft-lbs/cu. in.	70
Tg.	180°C.	

#### Example XV

To a solution of 27.4 grams 2,2-bis(4-hydroxyphenyl)propane (.12 mole), 160 cc. dimethylsulfoxide and 45 cc. benzene there were added 25.27 grams of a 53.28% aqueous KOH solution (0.24 mole). The mixture was refluxed as in the previous example for 5 hours for water removal and the anhydrous dipotassium salt of the 2,2-bis(4-hydroxyphenyl)propane was obtained dissolved in the dimethylsulfoxide.

The mixture was cooled and 23.04 grams 2,4-dichloronitrobenzene (0.12 mole) added. Some darkening and a rapid temperature rise to 70°C. were noted. After about 10 minutes at this temperature, the viscosity was noticeably increased. The mixture was held 3½ hours at about 80°C. then methyl chloride bubbled in for a short time. The reaction mixture was diluted with 40 cc. benzene and filtered through a fine filter to remove salt. The clear polymer solution was precipitated into alcohol in an agitated vessel, filtered, washed with alcohol and dried in a vacuum oven. Yield 36 grams (calculated 41.6).

The polymer had units of the formula



and a reduced viscosity of 0.49 (0.05 g./25 ml. CHCl<sub>3</sub> at 25°C.). A film molded at 190°C. was yellow and showed the following properties:

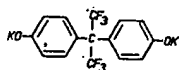
Tensile Modulus	320,000 psi.	
Tensile Strength	10,500 psi.	
Elongation to Break	5–50%	105
Pendulum Impact	5 ft-lbs/cu. in.	
Tg.	150°C.	

#### Example XVI

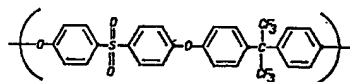
This example was conducted in essentially the same manner as Example I, employing as



one reactant, the dipotassium salt of hexafluorobisphenol having the structure:



- 5 which was made by reacting 33.63 grams of 2,2'-bis(hydroxyphenyl) 1,1,1,3,3,3 - hexafluoropropane (0.1 mole) with 21.06 grams (0.2 mole) of a 53.2% aqueous potassium hydroxide solution, in 150 ml. dimethylsulfoxide and 45 ml. benzene. After refluxing  
10 for 4.5 hours to azeotropically remove the water, the dipotassium salt of the hexafluorobisphenol was reacted with 25.42 grams of 4,4'-difluorodiphenylsulfone (0.1 mole) to obtain the polyether having units of the formula:  
15



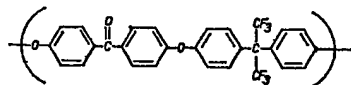
- The reaction was conducted at 120—130°C. for one hour after which the polymer was recovered, washed, and dried, securing 54.3 grams of a white granular powder. The  
20 reducer viscosity of the polymer in chloroform was 0.60 and the following mechanical properties of compression molded film samples were measured.

- 25 Tg. 205°C.  
Tensile Modulus 280,000 psi.  
Tensile Strength 9,500 psi.  
Elongation to Break 3—36%  
Pendulum Impact 60ft-lbs/cu. in.

- 30 The polymer was highly resistant to oxidation in that it did not discolor or change in physical properties after one month in a 225°C. air oven. It also showed substantially no change after 2 hours at 350°C. in a nitrogen atmosphere but did gel at 400°C. in  
35 about 2 to 3 hours.

#### Example XVII

- This example was run in the same manner as the previous example except that 4,4'-difluorobenzophenone was substituted for the  
40 4,4'-difluorophenylsulfone. The polymer had units of the formula:



- 45 and a reduced viscosity in chloroform of 0.68. It had the following mechanical properties, as measured on a compression molded film sample.

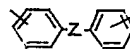
Tg.	175°C.	
Tensile Modulus	285,000 psi.	
Tensile Strength	10,500 psi.	50
Elongation	170%	
Pendulum Impact	200 ft-lbs./cu. in.	

It had equivalent oxidation and high temperature resistance to the polyether of the previous example.

We are now aware of British Patent Specification No. 1016245 which is generally concerned with thermoplastic polymeric materials consisting essentially of repeating units having the structure

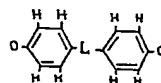


where Ar is a divalent aromatic residue which may vary from unit to unit in the polymer chain and in at least some of the units Ar has the structure I



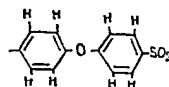
(1)

(where Z is an oxygen or sulphur atom or the residue of a 4,4'-bisphenol having the structure II



(II)

where L is —CO— or —SO<sub>2</sub>— and in any other units Ar is a residue of benzene, diphenyl, or a polynuclear aromatic hydrocarbon containing not more than two aromatic nuclei, so that in the divalent aromatic residues containing two benzene rings each benzene ring bears one of the valencies, and one or more of the aromatically bound hydrogen atoms in any of the divalent aromatic residues may be replaced by halogen atoms or alkyl or alkoxy groups containing from 1 to 4 carbon atoms. Accordingly we make no claim to polymeric material which consists essentially of repeating units having the structure



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Neither do we claim polymeric material as claimed in claim 1 of Specification No. 1016245 and which is substantially as described and illustrated by any one of the examples 1 to 15 inclusive.

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Subject to this disclaimer,  
WHAT WE CLAIM IS:—

1. A linear thermoplastic polyarylene polyether containing recurring units having the formula



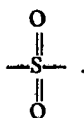
where E is the residuum of a dihydric phenol, as hereinbefore defined, and E' is the residuum of a benzenoid compound, as hereinbefore defined, having an inert electron withdrawing group in at least one of the positions ortho or para to the valence bonds, and where both of said residua are valently bonded to the ether oxygens through aromatic carbon atoms.

2. A linear thermoplastic polyarylene polyether as claimed in claim 1 wherein E is a polynuclear residuum in which both valence bonds to ether oxygens are attached to aromatic carbon atoms of different aromatic nuclei.

3. A substantially linear thermoplastic polyarylene polyethers as claimed in any one of claims 1 or 2 wherein E' is a mononuclear residuum in which both valence bonds to ether oxygens are attached to aromatic carbon atoms of the same aromatic nuclei and said inert electron withdrawing group is a monovalent group.

4. A linear thermoplastic polyarylene polyether as claimed in claim 1 or claim 2 wherein E' is a polynuclear residuum in which both valence bonds to ether oxygens are attached to aromatic carbon atoms of different aromatic nuclei connected together by a divalent inert electron withdrawing group.

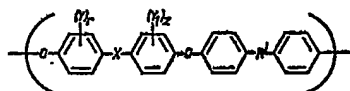
5. A linear thermoplastic polyarylene polyether as claimed in any one of claims 1, 2 or 4 wherein the divalent inert electron withdrawing group is the sulfone group,



6. A linear thermoplastic polyarylene polyether as claimed in any one of claims 1, 2 or 4 wherein the divalent inert electron withdrawing group is the carbonyl group,

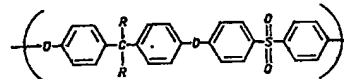


7. A substantially linear thermoplastic polyarylene polyether as claimed in claim 1 and containing recurring units having the formula



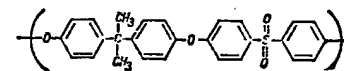
wherein X represents a bond between aromatic carbon atoms or a divalent connecting radical, R' represents a sulfone, carbonyl, vinyl, sulfoxide, azo, saturated fluorocarbon, organic phosphine oxide or ethylidene group, Y and Y<sub>1</sub> each represent halogen, alkyl groups having from 1 to 4 carbon atoms or alkoxy groups having from 1 to 4 carbon atoms, and where r and z are O or integers having a value from 1 to 4 inclusive.

8. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula

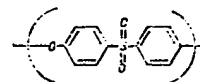


wherein R represents hydrogen, lower alkyl, lower aryl or a halogen substituted group thereof.

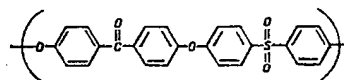
9. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



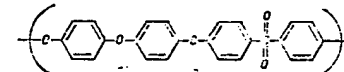
10. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



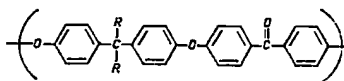
11. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



12. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula

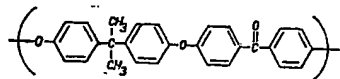


13. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula

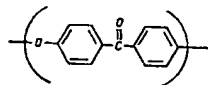


wherein R represents hydrogen, lower alkyl, lower aryl, or a halogen substituted group thereof.

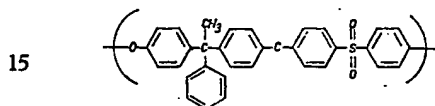
- 5 14. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



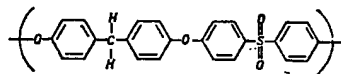
- 10 15. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



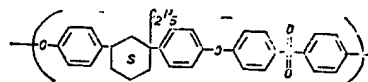
16. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



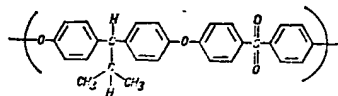
17. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



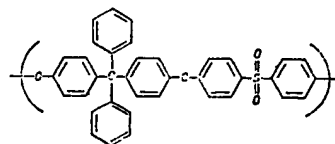
- 20 18. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



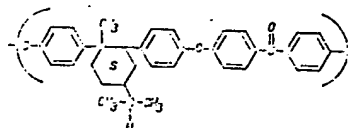
- 25 19. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



- 30 20. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula

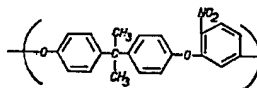


21. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula

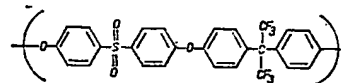


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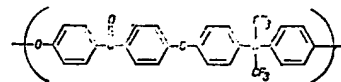
22. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



23. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



24. A linear thermoplastic polyarylene polyether as claimed in claim 1, and containing recurring units having the formula



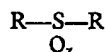
25. A linear thermoplastic polyarylene polyether substantially as hereinbefore described with particular reference to any of the Examples.

26. A process for preparing linear polyarylene polyethers which comprises reacting an alkali metal double salt of a dihydric phenol

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with a dihalobenzenoid compound in which each halogen is bonded to a benzene ring and having an inert electron withdrawing group in at least one of the positions ortho or para to the halogen atoms under anhydrous conditions and in the liquid phase of an inert, highly polar organic solvent.

27. The process for preparing linear polyarylene polyethers as claimed in claim 26 in which the polar organic solvent has the formula



in which each R represents a lower hydrocarbon group free of aliphatic unsaturation on the alpha carbon atom and, when connected together, represents a divalent alkylene group, and z is an integer from 1 to 2 inclusive.

28. A process as claimed in claim 26 or 27 wherein the reaction is conducted at a temperature above 100°C. and below the decomposition temperature of the reactants, the solvent and the polymer.

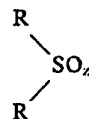
29. A process as described in any one of claims 26, 27 or 28 wherein the water content of the reaction mixture is maintained less than 0.5 per cent by weight.

30. A process as claimed in any one of claims 26 to 29 wherein a cosolvent for the polymer is present during the polymerization.

31. A process as claimed in claim 30 wherein the cosolvent is a halogenated benzene.

32. A process as claimed in any one of claims 26 to 31 in which the double alkali metal salt is made *in situ* by reacting a dihydric phenol with about stoichiometric amounts of an alkali metal hydroxide for a time and at a temperature sufficient to form the alkali metal double salt of the dihydric

phenol in the presence of an organic solvent having the formula



in which each R represents a monovalent lower hydrocarbon group and when connected together represents a divalent alkylene group and z is an integer from 1 to 2 inclusive, and thereafter removing the water from the said mixture before contacting the alkali metal double salt of the dihydric phenol with the dihalobenzenoid compound.

33. A process as claimed in claim 32 wherein the water is removed from the reaction mixture by the use of an azeotrope former with water.

34. A process as claimed in claim 33 wherein the water content of the reaction mixture is reduced to less than 0.5 per cent by weight of the azeotrope former.

35. A process as claimed in claim 34 wherein a cosolvent for the polymer is present during the polymerization.

36. A process as claimed in claim 34 wherein the solvent is dimethylsulfoxide.

37. A process for preparing substantially linear thermoplastic polyarylene polyethers as described with particular reference to any of the Examples.

38. A linear polyarylene polyether when prepared by a process as claimed in any one of claims 26 to 37.

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